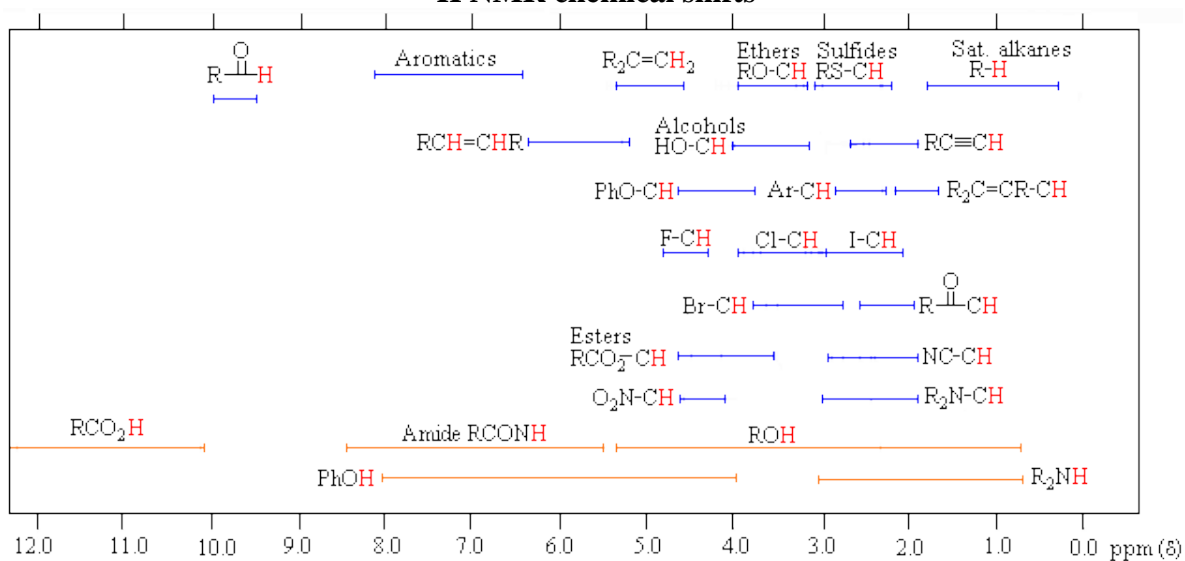




¹H NMR chemical shifts



CHE-334 questions

Part I: 5 of 7 questions (110 pts.)
 Part II: 3 of 5 questions (45 pts.)
 Total exam: 8 of 12 for 155 pts.

CHE-534 questions

Part I: 6 of 7 questions (120 pts.)
 Part II: 3 of 5 questions (45 pts.)
 Total exam: 9 of 12 for 165 pts.

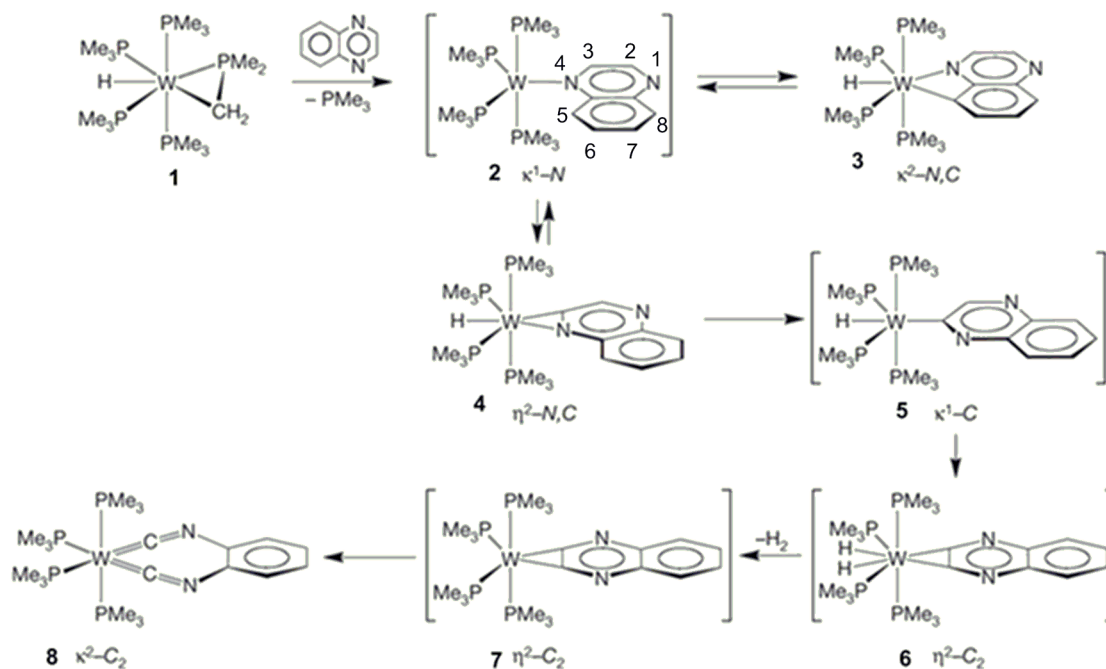
Part I: Questions from Class Presentations

CHE-334: Answer 5 of 7 questions. The first two are worth 25 points and the remaining questions are worth 20 points.

CHE-534: Answer 6 of 7 questions. All questions are worth 20 points.

1. The proposed mechanism for the recent seminal work on C-C bond cleaving of an unstrained aromatic ring is shown below (Aaron Sattler et al. [Nature](#)2010, 463, 523-526).

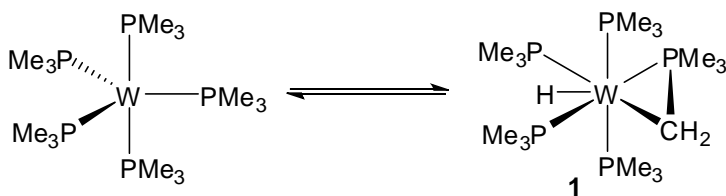
Answer 5 of the 6 parts of question 1.



a) The equilibria between **2**, **3** and **4** is a critical entry point to the ultimate goal of reaching complex **8**. In analyzing these two equilibria, **2** to **3** and **2** to **4**, what is the same about these reactions? What makes these processes different? Identify one unifying and one differentiating characteristic. (Do NOT make this more complicated than it is!)

b) Some complexes in the mechanism above have a κ^2 designation while others have a η^2 . What does κ^2 and η^2 describe?

c) The W reagent, **1**, could also exist as the trigonal bipyramidal structure on the left below. Provide a reason that the structure on the right is favored.



As reported in the article, the key novel reaction, the C-C bond cleaving step, occurs with the conversion of **6** to **8**.

d) How did the authors prove experimentally that the transformation of **6** to **7** was important for the formation of **8**?

e) Why might the process to form **7** be important before the W performs the critical C-C bond cleavage to form **8**?

f) The authors reported the following experimental information for **8**.

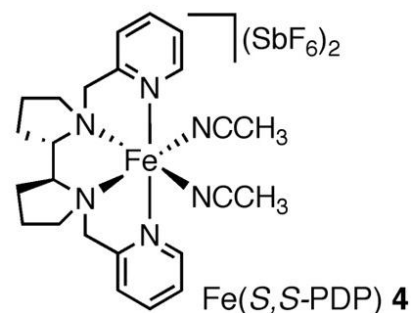
	<u>$^{13}\text{C NMR}$</u>	<u><i>IR, CN stretch</i></u>
<i>complex 8</i>	211.4 ppm	1709-1698 cm ⁻¹
<i>normal range for M-CN-R (isocyanide):</i>	151.8-238.7 ppm	2310-1670 cm ⁻¹

What does this say about the bonding relationship between the W-C? Briefly explain.

2. The article entitled, "A Predictably Selective Aliphatic C–H Oxidation Reaction for Complex Molecule Synthesis" by M. Christina White et al. ([Science 2007, 318\(5851\), 783-7](#)) described oxidation reactions with the complex shown below.

a) What is the oxidation state of the Fe?

b) Identify the X and L type ligands on the complex.



c) What is the total electron count of the Fe in **4**?

d) What is the coordination number and molecular geometry of the Fe in **4**?

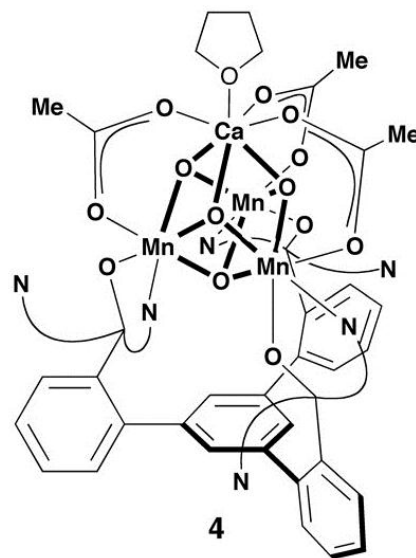
e) Draw the electronic orbital diagram for the Fe d orbitals. Include the correct number of electrons based on your answer to part a of this question. Label the d_{π} and d_{σ} orbital groups.

f) Although the mechanism of the oxidation processes catalyzed by **4** was unknown, if the substrate and/or oxidant did interact directly with the iron, i.e. inner sphere reactions, what would be the

mechanism of ligand substitution and what ligand(s) would be most likely to substitute? Why would this ligand be most likely to leave?

3. The authors of the recent article entitled, “A Synthetic Model of the Mn_3Ca Subsite of the Oxygen-Evolving Complex in Photosystem II” (Theodor Agapie et al. [Science](#) **2011**, *333*(6043), 733-736), detailed the synthesis of the metal cluster complex **4**. Answer 5 of the 6 parts in question 3.

a) The presenters of the article in class showed a method for calculating the approximate formal charge on each Mn in the cluster. Determine the charge by showing that calculation.



b) What analytical tool did the researchers use to determine the oxidation state of the Mn atoms in the metal cluster? How did they use this tool to determine the oxidation state?

c) Why do oxo or alkoxy ligands work well to stabilize high oxidation state metals?

d) What was the effect of adding Ca^{+2} to the Mn cluster?

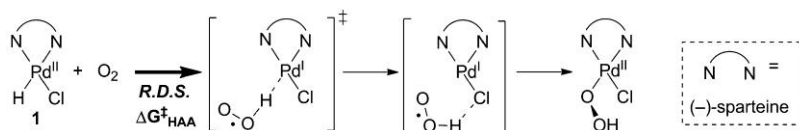
e) In the context of the photosystem II oxygen-evolving complex and its catalytic process that converts $2 \text{H}_2\text{O}$ to O_2 and 4H^+ 's, why is it necessary to have high oxidation state Mn?

f) If you were conducting this research, what do you see as the next important step to prove the validity of the Mn_3Ca metal cluster model as a mimic of photosystem II?

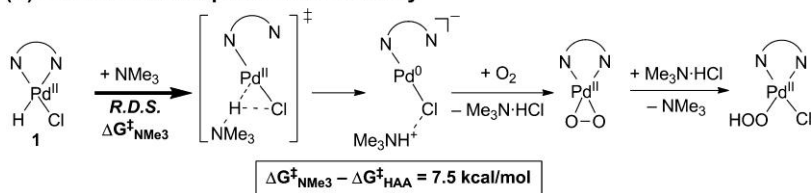
4. Answer the following questions about the article "Reaction of O_2 with [(-)-Sparteine]Pd(H)Cl: Evidence for an Intramolecular [H-L]+ "Reductive Elimination" Pathway" by Shannon S. Stahl et al. ([J. Am. Chem. Soc., 2011, 133, 13268–13271](#)), which we discussed on December 1, 2011.

a) The authors showed the following possible mechanisms (A and B, below) and postulated that the pathways could be differentiated by the effects of O_2 pressure/concentration on the reaction. Why did they see this as critical? Be as explicit as possible.

(A) H-Atom-Abstraction (HAA) Pathway



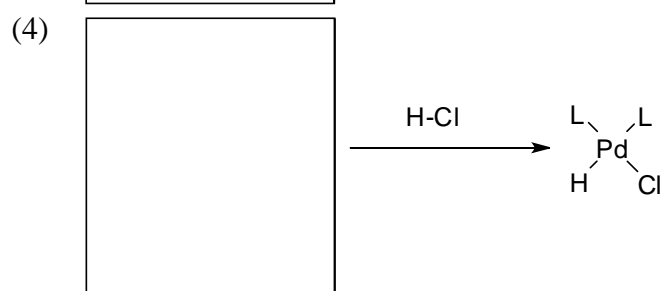
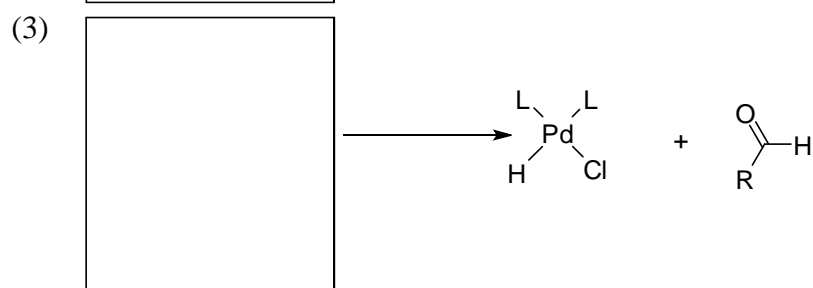
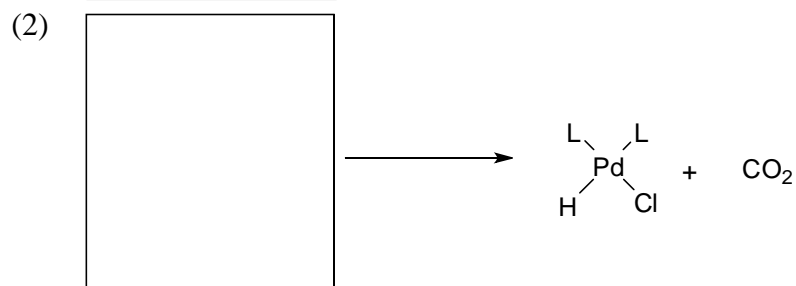
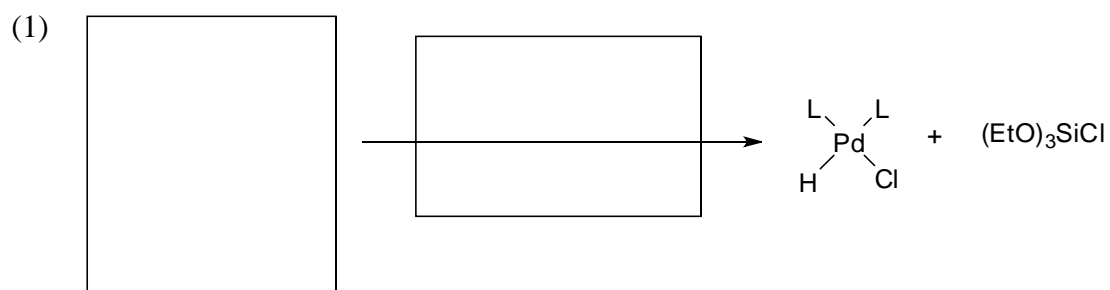
(B) External Base Deprotonation Pathway



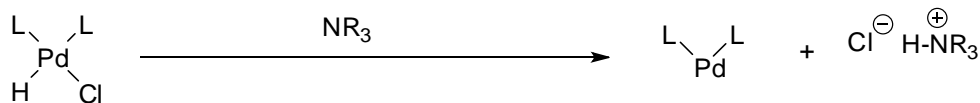
b) One of the key steps in their quest to understand O₂ reactions with (Sp)Pd(H)Cl was to actually generate (Sp)Pd(H)Cl that could then be studied experimentally. In the text, the authors describe basically four procedures that they explored and parts of these procedures are shown in the equations below. Provide the starting materials and reagents as requested *for three of the four equations* below. Identify the type of reaction process occurring in the three equations you answer

reaction to form (Sp)Pd(H)Cl

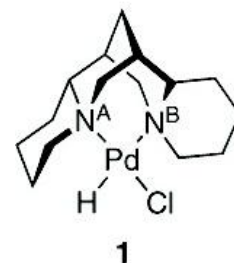
**type of
reaction
process**



c) As I described in class, there are actually two ways to see the sequence of events in the reductive elimination of a $L_2Pd(H)Cl$ complex to form L_2Pd and $ClHNR_3$. Draw both paths. Use electron flow arrows and/or text as necessary to explain your concept.



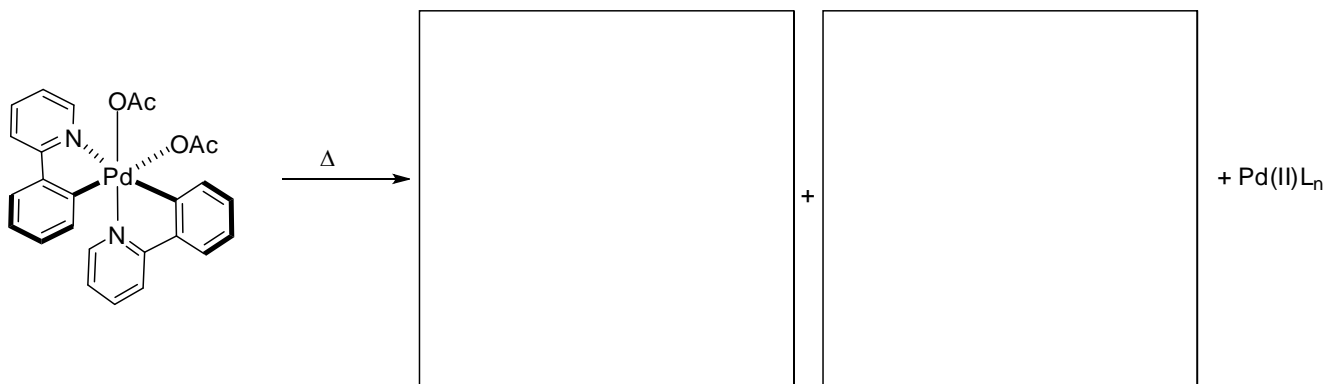
d) The authors of the paper computationally determined the $Pd-N_B$ bond to be longer than the $Pd-N_A$ bond in the $(Sp)Pd(H)Cl$ (Sp =sparteine) complex below. What is the likely reason for this difference?



e) Why was the lengthening of the $Pd-N_B$ bond critical in their proposal?

5. The following questions are based on the work of Melanie Sanford and co-workers as described in their recent article that we reviewed ([J. Am. Chem. Soc. 2009,131, 10974–10983](#)).

a) The reaction that was studied is shown below. Provide the **TWO POSSIBLE ORGANIC PRODUCTS** in the boxes to the right. (Note that the focus is on organic products because this course is ORGANOMETALLIC chemistry where the organo comes first!)



b) Although the authors proposed three mechanistic possibilities, they favored a two step process that first involved dissociation of one of the acetate ligands. The authors tried two experiments that demonstrated rapid exchange of one acetate ligand. Briefly describe one of these examples. Be sure to include an equation and the analytical tool that was used to identify the exchange.

Another experiment looked at the effect of solvent on the acetate ligand exchange process. The table below illustrates their results.

Table 2. Effect of Solvent on the Rate of Carboxylate Exchange from 7

Cc1ccc(cc1)N2C=CC=CC=C2Pd(O2CR)(O2CR)C3=CC=CC=C3
 $\xrightleftharpoons[\text{solvent}]{\substack{k_{rel} \\ 1 \text{ equiv } Bu_4N(OAc) \\ -38 \text{ } ^\circ C}}$
Cc1ccc(cc1)N2C=CC=CC=C2Pd(O2CR)(OAc)C3=CC=CC=C3

(R = C₉H₁₉)

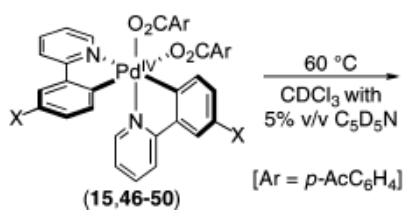
entry	solvent	ϵ	k_{rel}
1	toluene- <i>d</i> ₈	2.4	<0.1
2	acetone- <i>d</i> ₆	21	1.0 ± 0.1
3	CD ₃ CN	38	2.0 ± 0.2
4	CDCl ₃	4.8	19 ± 1

c) If the acetate ligand dissociation was the first step in the mechanism, what did the authors expect to see when changing the solvent polarity?

d) Based on the results in the table, what did the experiment show?

e) The article also reported on electronic effects of phenyl ring substitution on the reductive elimination. The results are shown below. What do these results say about the nature of the reductive elimination process and the role of the phenyl group?

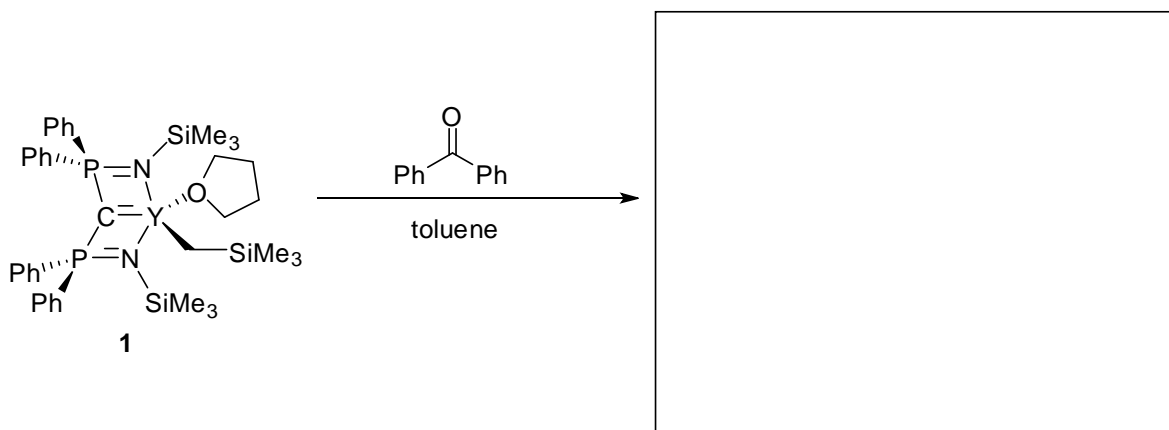
Table 5. k_{obs} for Reductive Elimination from $(\text{Arpy})_2\text{Pd}^{\text{IV}}[\text{O}_2\text{C}(p\text{-AcC}_6\text{H}_4)]_2$



Compound	k_{obs} ($\text{s}^{-1} \times 10^5$)
*OMe (46)	$\sim 3^a$
Me (47)	4.81
H (15)	20.0
F (48)	3.64
Cl (49)	36.9
*CF ₃ (50)	$\sim 320^a$

6. The following work was reported by Stephen Liddle and co-workers in the *Journal of the American Chemical Society* ([J. Am. Chem. Soc., 2010, 132, 14379–14381](#)).

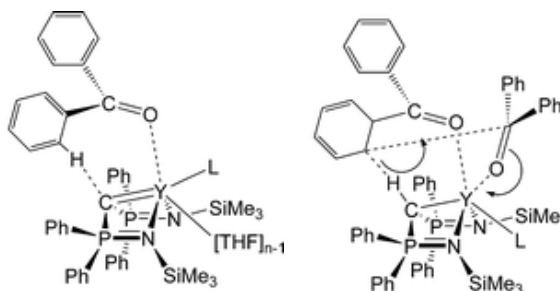
a) Provide the product and identify the type of mechanistic process shown below.



b) What is the generic name of the C=Y moiety?

c) In class we discussed two versions of organometallic structures with a C=M double bond. Provide the name of one of these and draw the electronic structure, i.e. the orbital interactions between the C and the M. Label the σ and π bond. Identify the polarization of the C and M in the example that you choose.

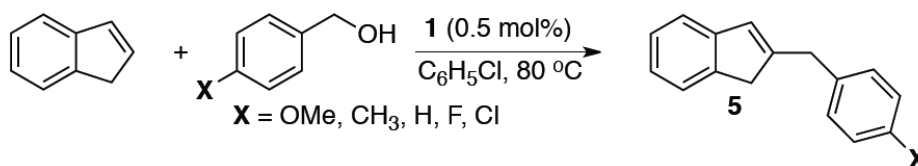
d) In one of the reactions studied with the new C=Y complex, the researchers proposed the key intermediates shown below. What experiment did they conduct to prove that these intermediates were important and were involved with the rate determining step in the process?



e) The intermediates shown above in part d illustrate a fundamental bonding interaction in chemistry discovered and described by Gilbert N. Lewis. In particular the interaction between O and Y are representative of this type of bonding interaction. Describe this interaction using classical chemistry terminology and briefly explain why the two atoms play their role.

7. In a recent report in *Science*, Chae S. Yi described a new reaction to couple alcohols and alkenes. Answer the following based on our discussion of this report. Chae S. Yi et al. [Science 2011, 333\(6049\), 1613-1616](#)). Answer 5 of the 6 parts in question 7.

Yi and co-workers reported studying the following reaction in their quest to understand the mechanism of the new reaction that they reported.



By altering X as shown, the researchers generated the Hammett plot below with the triangle dots relating to this particular experiment to form 5.

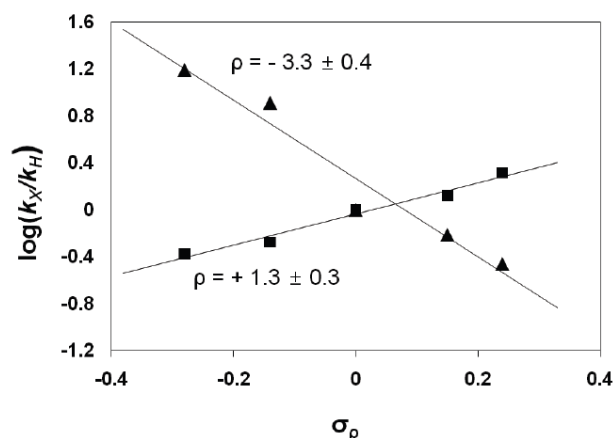
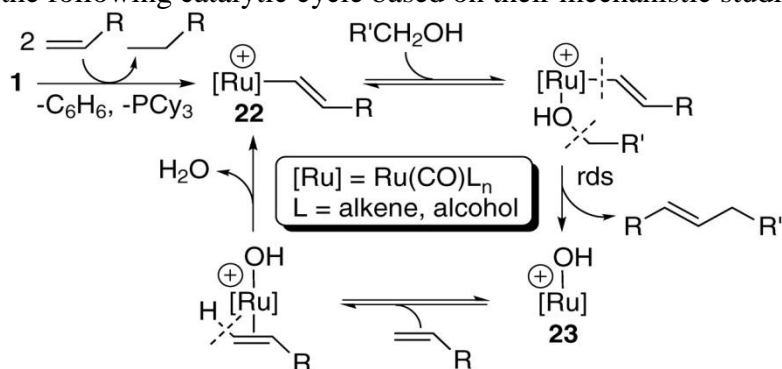


Figure S3. Hammett plot of the alkylation of indene with $p\text{-X-C}_6\text{H}_4\text{CH}_2\text{OH}$ ($\text{X} = \text{OCH}_3, \text{CH}_3, \text{H}, \text{F}, \text{Cl}$) (\blacktriangle), and $p\text{-Y-C}_6\text{H}_4\text{CH}=\text{CH}_2$ ($\text{Y} = \text{OCH}_3, \text{CH}_3, \text{H}, \text{F}, \text{Cl}$) with PhCH_2OH (\blacksquare).

Note: triangles are associated with the substituents listed above in the order listed from left to right.

a) What does the trend from the Hammett plot show and what conclusion was drawn about the mechanism of the reaction?

The authors propose the following catalytic cycle based on their mechanistic studies.



b) As noted in the center of the figure, all the Ru complexes are believed to contain a CO ligand, along with alkenes and alcohols. Based on our course discussions, can you suggest another experiment that might be conducted to determine the electronic nature of the Ru metal? Briefly explain what trends might be expected and what they might say about the electronic nature of the Ru metal.

The mechanism shown in the article is intentionally abbreviated as the limited mechanistic work does not allow a complete description. Nevertheless, it is possible to propose more details.

c) What is happening in the first step in the main catalytic cycle, i.e. when **22** adds $R'CH_2OH$?

d) The next step is the critical C-C bond forming step. Propose details for this process that forms **23** and $R-CH=CH-CH_2-R'$. Draw all intermediates and label each step by the type of process occurring.

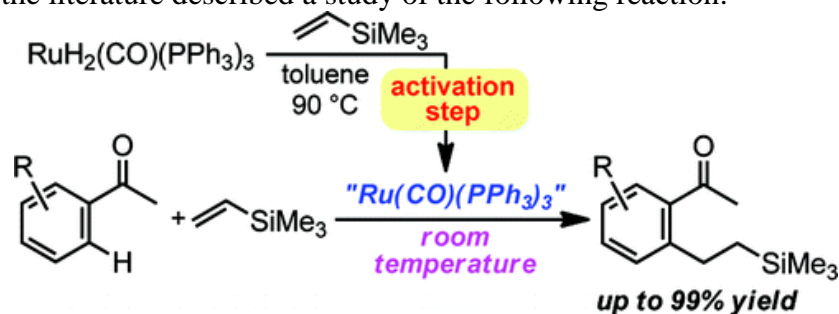
e) What happens with **23**'s reaction with $\text{H}_2\text{C}=\text{CH-R}$?

f) Finally the last step in the proposed catalytic cycle could be seen as two steps. Draw these two steps. (Hint: the two steps do change Ru's oxidation state, but because they are complimentary there is no net change in Ru's oxidation state.)

Part II: General Questions

All students complete 3 of 5 questions in this part. Each are worth 15 points.

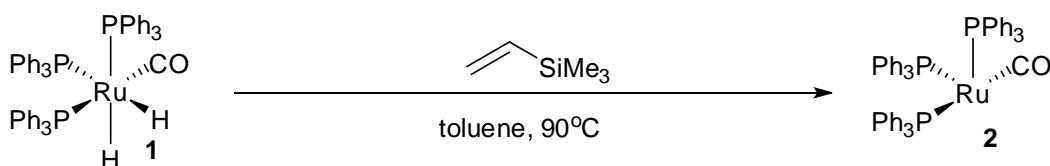
A recent article in the literature described a study of the following reaction:



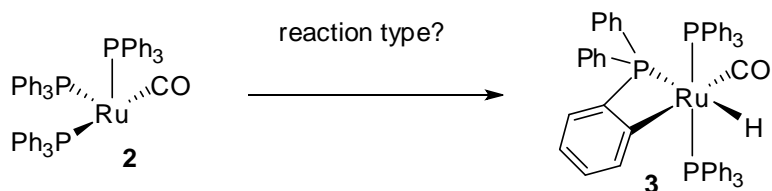
Shinji Murai et. al. [J. Am. Chem. Soc., 2010, 132, 17741–17750](#).

The next two questions examine these results in more detail.

8. a) As indicated, the first step of the catalytic process was an activation step for the catalyst, i.e. the transformation of **1** to **2** (below). Propose a mechanism for the activation process. Include all intermediates and label all steps by the type of process occurring.



b) The Ru(0) complex **2** is actually not stable and undergoes the following reaction. What is this reaction type?

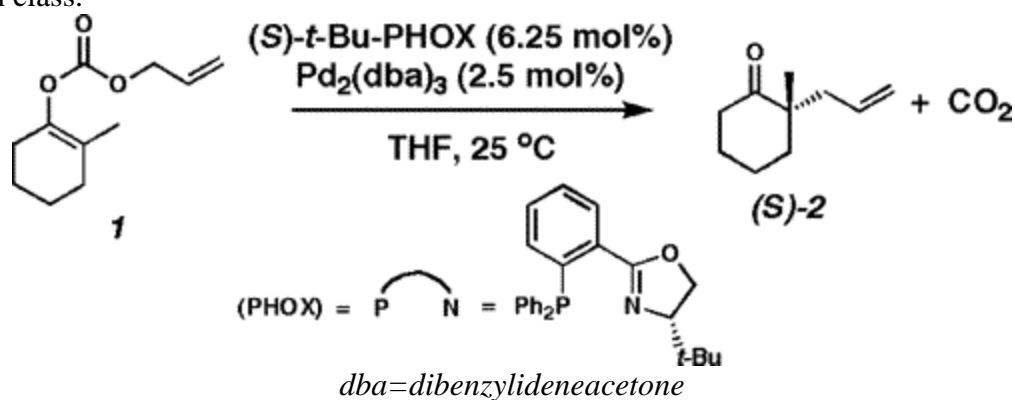


9. a) The authors were able to characterize **3** by NMR. In particular they found a signal for the Ru-H in the ^1H NMR. What chemical shift (δ) in the ^1H NMR spectrum would you expect for the Ru-H signal?

b) The splitting pattern reported for the Ru-H proton was dt or a doublet of triplets. Explain this splitting by describing all the coupling partners that generate the dt.

c) The ^{31}P NMR had two signals: $\delta -35.3$ (t, $J_{\text{PP}} = 15.2$ Hz) and 52.1 (d, $J_{\text{PP}} = 15.2$ Hz) ppm. What does the chemical shift say about the difference in the two phosphorus atoms? Suggest an assignment for the signals to a particular P in complex **3**.

10. The following reaction was studied by Brian Stoltz and co-workers and the results of the study were reported in the *Journal of the American Chemical Society* ([JACS 2003, 129\(39\), 11876-7](#)) and discussed in class.



a) The first half of the process involves taking **1** to an η^3 -allyl Pd complex. Propose steps to convert **1** to such a complex. Draw all intermediates and label each step by the type of reaction occurring.

b) There are two basic paths that can lead to (S)-**2** from the η^3 -allyl Pd complex. Show one of those two paths.

c) The product is chiral, but **1** lacks a chiral center. Describe or show figures that illustrate how chirality is induced in the final product (*S*)-**2**.

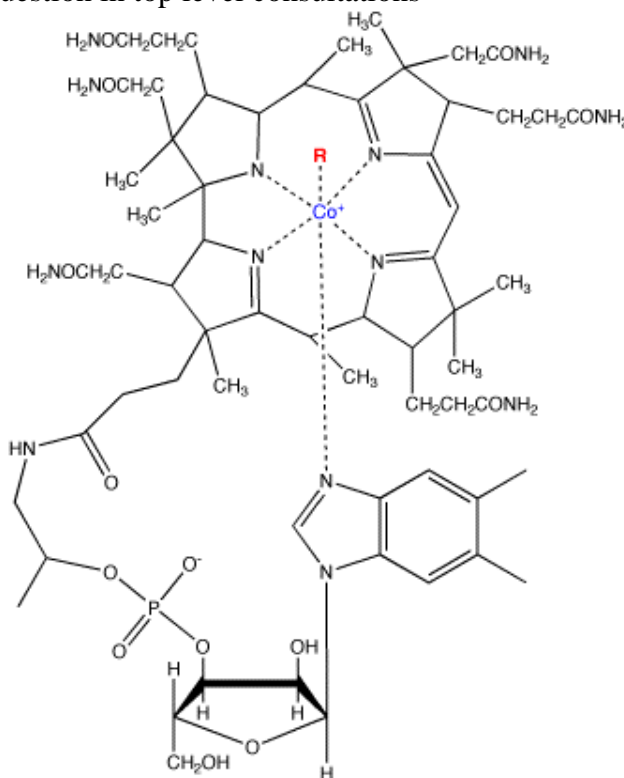
11. Analyze the structure of vitamin B₁₂ or cobalamin, the most complex of all vitamins, and drawn below. In the figure, R can be CH₃, CN or OH

a) Identify the ligands as either X or L type.

b) Identify the oxidation state of the cobalt (assume R to be one of the ligands listed above).

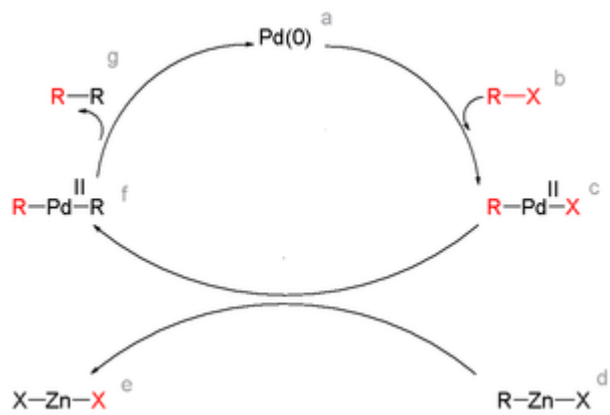
c) Determine the total electron count at cobalt.

Dr. B approved of this question in top level consultations



12. On the first day of lecture, I showed the 2010 Nobel Prize in Chemistry announcement. The award was made to Richard Heck, Akira Suzuki, and Ei-ichi Negishi for their contributions to palladium-catalyzed cross coupling reactions in organic synthesis. The catalytic cycles for all three of these processes are shown below. *Identify the mechanistic steps in two of the three.*

a) Mizoroki-Heck reaction



a to c=

c to f=

f to a=